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DESCRIPTION

PROCESS FOR PRODUCING MESOPHASE PITCH BASED ACTIVE
CARBON FIBER, MESOPHASE PITCH BASED ACTIVE CARBON
FIBER AND ELECTRIC DOUBLE LAYER CAPACITOR

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DETAILED DESCRIPTION OF THE INVENTION

(TECHNICAL FILED OF THE INVENTION)

The present invention relates to a production of a
mesophase pitch based active carbon fiber suitable for use
10   in an electrode material of an electric double layer
capacitor. More particularly, the present invention
relates to a process for producing an active carbon fiber,
which, when used as an electrode material, is capable of
realizing large charge and discharge capacities per weight
15   and per volume, and also relates to such an active carbon
fiber and an electric double layer capacitor including an
electrode in which the active carbon fiber is used.

(BACKGROUND ART)

20   In recent years, new electronic equipments such as a
portable telephone and a notebook-size personal computer
have been developed in succession. In accordance with the
development competition intended to reduce the volume and
weight of these goods and to make them portable, the
25   miniaturization, while ensuring high performance, of IC

memory, microcomputer and other items built therein is being promoted.

In this connection, elements such as IC memory, and microcomputers have the danger of causing the electronic

5   equipments to suffer from misfunctioning such as memory cancellation or operation termination at the time of instantaneous power cut.

Actually, computer equipments, unless appropriate measures are taken, suffer from operation termination and

10   memory loss only if a voltage drop as small as 10 to 20% is continued for a short period of 0.003 to 0.02 second with the result that the functions of the electronic equipments are paralyzed.

As a countermeasure, for example, a Ni-Cd battery or

15   an aluminum electrolytic condenser has been employed as a backup power source. However, such a backup power source has not been satisfactory from the viewpoint of range of use temperature, charge and discharge cycles, capacity, charge and discharge rapidity and cost.

20   An electric double layer capacitor has been developed to meet market needs in the above circumstances.

At the initial stage, active carbon was commonly used as an electrode material therein. However, recently, attention is being drawn toward an electric double layer

capacitor in which use is made of an active carbon fiber having an increased specific surface area.

The application thereof to not only conventional small-power fields but also large-capacity fields, for

5   example, an auxiliary power source for the battery of electric automobiles is being studied. The current stage is such that some passenger cars on which capacitors are mounted for the purpose of charging the regenerative kinetic energy produced at the time of deceleration to the

10 capacitor and contrarily discharging the energy at the time of acceleration to thereby support the engine output are shown as reference exhibits.

The history of researches on the electric double layer goes back to Helmholtz, as old as 1879. Generally, when

15 two phases different from each other are brought into contact, positive and negative charges are arranged at the interface, with a small interval therebetween. The charge distribution produced at the interface is called the electric double layer.

20 The electric double layer capacitor is one in which voltage is applied to the electric double layer to thereby accumulate charges. However, a prolonged period of time has been taken for the practical use thereof. It was only the beginning of the 1980s when the development of a

condenser with a large capacity of Farad unit in which this principle was introduced was realized.

The electric double layer capacitor is a large-capacity condenser in which an electric double layer formed at an interface of an electrode and an electrolyte is utilized. The charging and discharging effected with the electric double layer capacitor are not accompanied by any chemical reaction made in conventional secondary batteries. Therefore, the internal resistance of the electric double layer capacitor is extremely low as compared with those of secondary batteries, so that a large-current discharging can be realized. Further, the electric double layer capacitor has the characteristic that there is no limit in charging and discharging frequency.

However, the most serious drawback of the electric double layer capacitor resides in that the energy density thereof is extremely low as compared with those of secondary batteries. Various investigations are now being conducted in order to accomplish an improvement in this respect.

Electric double layer capacitors are largely divided into two types, namely the one in which use is made of an organic electrolyte comprising an organic polar solvent such as propylene carbonate and, dissolved therein, an electrolytic substance such as lithium perchlorate or a quaternary ammonium salt and the other in which use is made

of an electrolyte composed of an aqueous solution such as aqueous solution of sulfuric acid or an aqueous solution of potassium hydroxide.

In the use of the electrolyte composed of an aqueous solution, the capacity of the capacitor can be increased to about 1.3 to 2 times that exhibited in the use of the organic solvent electrolyte, and the internal resistance can be lowered to 1/5 - 1/10 of that exhibited in the use of the organic solvent electrolyte.

The reason for the capability of lowering the internal resistance in the use of the electrolyte composed of an aqueous solution is attributed to low electrical resistance of the aqueous solution electrolyte. However, the use of the aqueous solution electrolyte is disadvantageous in that the voltage can be increased only to about 1 V with the result that the quantity of accumulated energy per volume is small.

On the other hand, in the use of the organic solvent electrolyte, the voltage of the electric double layer capacitor can be increased to a maximum of 3 V or more to thereby enable increasing the quantity of energy stored per volume of capacitor (quantity of stored energy determined by the formula: $1/2CV^2$ wherein C represents the capacity of capacitor and V represents the voltage). Therefore, the organic solvent electrolyte is advantageous over the

aqueous solution electrolyte from the viewpoint of an increase of energy density per volume.

With respect to the electrode material for use in the electric double layer capacitor, active carbon or active carbon fiber having a large specific surface area is considered to be the most suitable therefor, and, in various fields, investigations for optimization of carbon material are being promoted vigorously.

The electrode material for use in the electric double layer capacitor is generally produced from active carbon having a large specific surface area, which is obtained by providing a hardly graphitizable carbon material (carbon material whose graphitization is difficult, known as a hard carbon) such as coconut husk, coal or a phenolic resin as a raw material and subjecting the same to gas activation generally using, for example, steam or carbon dioxide.

In the electric double layer capacitor in which this active carbon is used as an electrode material, pores produced by the carbon-removing phenomenon attributed to a reaction between the carbon material and steam or carbon dioxide increase the interface at which the electric double layer is formed to thereby enable increasing the charge and discharge capacities per weight.

However, generally, for obtaining an electrode for use in an electric double layer capacitor having a large

discharge capacity per weight, it is requisite to employ an active carbon having a specific surface area, as measured by the BET method, of at least 2000 m^2/g. This active carbon requires activation condition wherein the activation yield

5   is as low as 20% by weight or less, thereby involving the problem of not only increasing the production cost for active carbon to be obtained but also causing the carbon material per se to have such a low bulk density that the bulk density of the electrode material cannot be enhanced.

10   According to measurements conducted by the inventor, the discharge capacity, in an organic solvent, of the electrode material composed of an active carbon prepared from the above hardly graphitizable carbon material as a raw material and having a BET specific surface area of 2000

15   m^2/g is only about 30 F/g. This value is below the value expected from the above specific surface area.

        This is considered to suggest that not all the specific surface area measured by the BET method is utilized in the formation of the electric double layer.

20   With respect to the production of an active carbon, the method of activating a carbon fiber in the presence of an alkali metal compound in order to increase the specific surface area thereof (hereinafter referred to as "alkali activation") was proposed (see Japanese Patent Laid-open

25   Publication No. 1(1989)-139865).

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Further, attempts have been made to apply this technology to a graphitizable carbon material such as a carbon material obtained by carbonizing pitch, especially mesophase pitch. For example, Japanese Patent Laid-open

5 Publication No. 5(1993)-247731 discloses the production of an active carbon fiber of large specific surface area (especially, at least 200 m^2/g) through a process comprising first spinning a pitch containing mesophase in a proportion of at least 50% (hereinafter may be generically

10 referred to as "mesophase pitch") to thereby obtain a pitch fiber, subsequently infusibilizing/carbonizing the obtained pitch fiber to thereby obtain a carbon fiber (hereinafter may be generically referred to as "mesophase pitch based carbon fiber") and thereafter activating the

15 carbon fiber in the presence of alkali.

Still further, in recent years, attempts have been made to use the active carbon fiber obtained by activating a graphitizable carbon material in the presence of alkali as an electrode material for use in an electric double layer

20 capacitor. For example, Japanese Patent Laid-open Publication No. 5(1993)-258996 proposes an electrode for electric double layer condenser, obtained by first activating a mesophase pitch based carbon fiber in the presence of alkali to thereby obtain an active carbon fiber

25 having a specific surface area of at least 3000 m^2/g,

subsequently deliming the active carbon fiber with water or an acid, next pulverizing the delimed carbon fiber to a degree such that no fibrous form remains and thereafter molding the powder.

5 However, the production of a mesophase pitch based carbon fiber by alkali activation involves the problem that the activation yield is lowered by providing a large specific surface area and that, in the use as an electrode material of electric double layer capacitor, the bulk

10 density thereof is low to thereby lower the charge and discharge capacities per volume.

The inventor et al., for overcoming the above problem, have proposed an electric double layer capacitor in which an active carbon fiber having a specific surface area of

15 500 to 2000 m^2/g, obtained by alkali activation of a mesophase pitch based carbon fiber, is used as an electrode material (see Japanese Patent Laid-open Publication No. 10(1998)-121336). Also, they have proposed an electric double layer capacitor in which an active carbon fiber of

20 specified pore distribution, obtained by milling a mesophase pitch based carbon fiber produced by a specified method and thereafter conducting alkali activation of the powder, is used as an electrode material (see Japanese Patent Laid-open Publication No. 11(1999)-222732).

These active carbon fibers are advantageous in that, in the use as an electrode material, high charging and discharging performance can be exhibited as compared with that of conventional active carbon fibers even if the specific surface area thereof is small, so that the charge and discharge capacities per volume can also be increased. However, the current situation is such that further enhancement of charging and discharging performance, especially increase of the charge and discharge capacities per weight and per volume, is desired with respect to the electric double layer capacitor including the electrode composed of these active carbon fibers as well.

(OBJECT OF THE INVENTION)

The present invention has been made with a view toward solving the above problems of the prior art. Therefore, an object of the present invention is to provide a process for producing an active carbon fiber which, when used as an electrode material, not only has a small specific surface area to thereby enable realizing a high bulk density but also exhibits excellent charging and discharging performance, especially capable of realizing large charge and discharge capacities per weight and per volume. Another object of the present invention is to provide such an active carbon fiber, and a further object of the present

invention is to provide an electric double layer capacitor including the electrode made by using the active carbon fiber.

(SUMMARY OF THE INVENTION)

The process for producing a mesophase pitch based active carbon fiber according to the present invention comprises the steps of:

(I) carbonizing a mesophase pitch based infusibilized fiber at 600 to 900°C,

(II) activating the thus obtained carbon fiber with alkali, and

(III) immersing the thus obtained mesophase pitch based active carbon fiber in an electrolyte and subjecting the immersed mesophase pitch based active carbon fiber to such a charge and discharge treatment that a voltage gradually increased until exceeding 2.5 V is applied at a constant current density to the mesophase pitch based active carbon fiber so that an electric double layer is formed at an interface of the mesophase pitch based active carbon fiber and the electrolyte to thereby effect a charging and thereafter a discharging is effected at a constant current density.

In the process for producing a mesophase pitch based active carbon fiber according to the present invention, it

is preferred that the active carbon fiber obtained in the step (II) have a BET specific surface area of 30 to 1200 m^2/g, especially 30 to 1000 m^2/g, and still especially 50 to 850 m^2/g. Further, the active carbon fiber obtained in

5   the step (II) preferably has an average pore radius, calculated from t-plot of a nitrogen adsorption isotherm, of 0.2 to 1 nm, still preferably 0.6 to 1 nm.

Moreover, in the step (III) in the process for producing an active carbon fiber according to the present

10   invention, the charging is preferably performed by applying a voltage gradually increased to 3.5 V in the electrolyte.

The active carbon fiber for use in an electrode of an electric double layer capacitor according to the present invention is characterized in that it is produced by the

15   above process.

It is preferred that the active carbon fiber of the present invention have a BET specific surface area of 30 to 1200 m^2/g, especially 30 to 1000 m^2/g, and still especially 50 to 850 m^2/g. Further, the active carbon fiber

20   of the present invention preferably has an average pore radius, calculated from t-plot of a nitrogen adsorption isotherm, of 0.2 to 1 nm, still preferably 0.6 to 1 nm.

Moreover, preferably, the BET specific surface area and the average pore radius after the step (III) do not

25   significantly different from those before the step (III).

The electric double layer capacitor of the present invention is characterized by including an electrode comprising the above mesophase pitch based active carbon fiber.

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(BRIEF DESCRIPTION OF THE DRAWING)

Fig. 1A shows a schematic perspective view of a preferred embodiment of electric double layer capacitor according to the present invention;

10   Fig. 1B shows a plan view of the electric double layer capacitor shown in Fig. 1A; and

Fig. 1C shows a sectional view taken in the direction of the arrow along the line C-C in Fig. 1B.

15   (DETAILED DESCRIPTION OF THE INVENTION)

The present invention will be described in greater detail below.

The process for producing a mesophase pitch based active carbon fiber according to the present invention

20 comprises:

(I) a carbonization step of carbonizing a mesophase pitch based infusibilized fiber at a specified temperature to thereby obtain a mesophase pitch based carbon fiber,

(II) an activation step of activating the thus obtained carbon fiber in the presence of alkali to thereby obtain a mesophase pitch based active carbon fiber, and

(III) a charge and discharge treatment step of

5 subjecting the thus obtained active carbon fiber to a specified charge and discharge treatment.

Each of the steps of the process of the present invention will be described at length below.

Carbonization step (I)

10 The mesophase pitch based infusibilized fiber for use as a starting material in the step (I) of the present invention can be produced by spinning mesophase pitch and infusibilizing the spun mesophase pitch (pitch fiber).

1) Pitch as starting material:

15 Although any of mesophase pitches, irrespective of being produced from petroleum or coal, can be used without any particular limitation as long as they are spinnable, it is preferred that this mesophase pitch contain an optically anisotropic phase in a proportion of at least 50%.

20 An active carbon fiber having a pore structure suitable for an electrode material of an electric double layer capacitor can be obtained from the mesophase pitch by converting it to a mesophase pitch based carbon fiber and activating the mesophase pitch based carbon fiber in

the presence of alkali as described below, although the reason therefor is not apparent.

2) Spinning method:

The spinning of the mesophase pitch can be performed by any of the conventional spinning methods. Examples of the spinning methods include the melt spinning, centrifugal spinning and vortex spinning. The melt-blowing spinning method is especially preferably employed.

The orientation of graphite layer planes in the interior of the fiber is important with respect to the mesophase pitch based carbon fiber. The degree of this orientation can mostly be controlled during the spinning step by the pitch viscosity, spinning speed, cooling rate, nozzle structure, etc.

In the alkali activation, it is considered to be an important factor that an alkali metal compound widens spacing of graphite layers and intercalates thereinto. In order to effectively promote the activation, it is preferred that edges of the graphite layers be exposed on the fiber surface so as to make an alkali metal compound easily enter inside from between the edges.

Further, the orientation structure of graphite layer planes is presumed to also have an influence on the activation yield.

The melt-blowing spinning method can be stated as being preferable from the collective viewpoint taking into account not only the above but also the production costs inclusive of construction and operating costs for spinning

5 apparatus and the quality matter inclusive of the control of fiber diameter.

This melt-blowing spinning method is especially suitable to the production of a carbon fiber mass with the form of a mat or a felt.

10 3) Infusibilization:

The pitch is a thermoplastic organic compound, so that, for conducting thermal treatment (carbonization) with allowing the same to maintain its fibrous form, infusibilization must be carried out after spinning.

15 This infusibilization, although can be effected continuously in the liquid or gas phase by customary techniques, is generally carried out in an oxidative atmosphere of air, oxygen, NO_2 or other gas.

For example, the infusibilization in air is performed

20 under such conditions that the average temperature rising rate is in the range of 1 to 15°C/min, preferably 3 to 12°C/min, and that the infusibilization temperature is in the range of 100 to 350°C, preferably 150 to 300°C.

If a pitch fiber spun, not having undergone

25 infusibilization, is directly mixed with an alkali metal

compound homogeneously and subjected to thermal treatment, the pitch fiber is re-melted in the heating step with the unfavorable result that the orientation of graphite layer planes formed in the spinning step is disordered and, in
5 extreme instances, the fibrous form is lost.

In the carbonization step (I) of the present invention in which the thus obtained mesophase pitch based infusibilized fiber is carbonized, the conditions thereof are not particularly limited as long as a carbon fiber from
10 which an active carbon fiber having properties suitable for an electrode material of electric double layer capacitor can be produced by the alkali activation step (II) and charge and discharge treatment step (III) described below can be provided. Accordingly, the carbonization of pitch
15 fiber may be conducted in customary conditions, for example, in an inert gas such as nitrogen at 350 to 2000°C, but is preferably carried out in an inert gas at 600 to 900°C, especially 650 to 800°C, from the above viewpoint.

Mesophase pitch based carbon fiber having been
20 carbonized at temperatures which are outside the above carbonization temperature range tends to decrease the proportion of small pores in the mesophase pitch based active carbon fiber obtained by the alkali activation step (II) described later. The use of this active carbon fiber
25 may fail to attain an exertion of satisfactory charge and

discharge capacity increasing effect in the subsequent

charge and discharge step (III) as described later.

More specifically, when the active carbon fiber from

the mesophase pitch based carbon fiber having been

5   carbonized at temperatures which are outside the above

carbonization temperature range is used in an electrode of

electric double layer capacitor, it is difficult, even if

the charge and discharge step (III) is performed by

increasing the charging voltage to 3.5 V, to attain such

10   a satisfactory charge and discharge capacity increasing

effect that the charge and discharge capacities per weight

at the charging at a constant current density with the

voltage increased to 2.5 V can be increased as much as at

least 10% when the specific surface area is in the range

15   of 30 to 1000 m^2/g and as much as at least 3% when the specific

surface area exceeds 1000 m^2/g and is up to 1200 m^2/g.

When the carbonization temperature exceeds 900°C,

unfavorably, not only does the graphite structure of the

carbon fiber grow to an extent beyond necessity to thereby

20   extremely retard the activation velocity with the result

that the reaction requires a prolonged period of time and

the carbonization cost is increased.

On the other hand, when the carbonization temperature

is below 600°C, although the progress rate of activation

25   is high, substantially no increase of charge and discharge

capacities by the charge and discharge treatment step (III) is recognized. Thus, unfavorably, the specific surface area must be enlarged for increasing the charge and discharge capacities to thereby invite lowering of

5 activation yield and cost increase.

Further, the lowering of activation yield is accompanied by lowering of the bulk density to thereby decrease the charge and discharge capacities per volume as well.

10 An active carbon fiber suitable for use in an electrode material can be obtained from the thus obtained mesophase pitch based carbon fiber, even if it remains in the form of a mat or a felt, by the activation step (II) and charge and discharge step (III) described later.

15 4) Milling:

Milling can be performed prior to the activation step (II) in order to effect homogeneous mixing with an alkali metal compound (activation auxiliary) in the activation step (II) and to increase the uniformity of specific surface

20 area and the bulk density of active carbon fiber after the activation reaction.

In the milling, the particle size in terms of average particle diameter as measured by laser diffractometry is preferably in the range of 5 to 50 μm, still preferably 10

25 to 30 μm.

When the average particle diameter exceeds 50 μm, it is likely that advance of the activation reaction into the internal part of particles is difficult and that the bulk density of the electrode material cannot be increased,

5 sufficiently. On the other hand, when the average particle diameter is extremely small below 5 μm, it is likely that control of the activation reaction and washing, after activation, etc. become difficult.

The milling can be effectively performed by the use

10 of a high-speed rotary mill such as Victory mill, a jet mill or the like. Although the milling can also be effected by Henschel mixer, a ball mill, grinding and the like, these are not preferable because a pressure is exerted along the direction of fiber diameter to thereby increase the

15 occurrence of cracking along the direction of fiber axis and lower the activation efficiency and homogeneity.

Further, these require a prolonged period of time in the milling, and hence can hardly be stated as being suitable milling means.

20 For example, the method in which fibers are chopped by rotating a rotor equipped with a blade at a high speed is suitable for highly efficient milling.

The fiber length can be controlled by regulating the rotating speed of the rotor, the blade angle, etc.

In the activation step (II) of the present invention, the thus obtained mesophase pitch based carbon fiber is activated in the presence of alkali.

Activation step (II)

5 Examples of the alkali metal compound for use in the activation step (II) of the present invention include potassium hydroxide, potassium carbonate, potassium nitrite, potassium sulfate and potassium chloride. Of these, potassium hydroxide is especially preferred.

10 The alkali metal compound is preferably used in a weight ratio to carbon fiber of 0.5 to 5, still preferably 1 to 4.

When the ratio of alkali metal compound is below 0.5, it is likely for the efficiency of pore formation to become

15 low. On the other hand, the addition thereof in excess of 5 is unfavorable from the viewpoint of not only cost increase for post-treatment but also the maintenance and safety of apparatus therefor.

The activation step (II) can be carried out, for

20 example, by homogeneously mixing the carbon fiber with the alkali metal compound in the above weight ratio and thereafter heating the mixture in an inert gas such as nitrogen at 500 to 900°C, preferably 600 to 800°C.

When the activation temperature is lower than 500°C,

25 the advance of the reaction is restrained. On the other

hand, exceeding 900°C is unfavorable from the viewpoint of precipitation of metallic potassium and corrosion of apparatus.

5 The danger attributed to the alkali metal remaining after the activation can be reduced by, for example, treating in an atmosphere of inert gas containing carbon dioxide at a temperature not greater than the activation reaction temperature after the completion of the activation reaction.

10 After the activation, the thus obtained mesophase pitch based active carbon fiber is subjected to cooling of the reaction mixture to room temperature, removal of unreacted alkali metal compound by, for example, washing with water and the charge and discharge step (III). The

15 mesophase pitch based active carbon fiber has a specified surface structure, for example, specified specific surface area and pore distribution.

1) Specific surface area of active carbon fiber:

It is preferred that the active carbon fiber obtained

20 by the activation step (II) of the present invention have a specific surface area of 30 to 1200 m^2/g, especially 30 to 1000 m^2/g, and still especially 50 to 850 m^2/g.

Namely, according to the observation of the inventors, the smaller the specific surface area of the active carbon

25 fiber, the higher the ratio of increase of charge and

discharge capacities attained by the charge and discharge step (III) described later (see the charge and discharge capacities after the charge and discharge treatment step in Examples of this specification).

5   There is a correlation, if not univocal, between the absolute value of the charge and discharge capacities and the specific surface area. Thus, a specific surface area of less than 30 m^2/g is not preferable because, even if the charge and discharge capacities are satisfactorily

10 increased in the charge and discharge step (III), the value thereof is as small as 20 F/g or less.

     On the other hand, when the specific surface area exceeds 1000 m^2/g, the effect of increasing charge and discharge capacities in the charge and discharge treatment

15 step (III) is suppressed. Further, when the specific surface area exceeds 1200 m^2/g, the increase of charge and discharge capacities that can be expected on the basis of specific surface area cannot be realized. More specifically, when this active carbon fiber is used in an

20 electrode of electric double layer capacitor, it is difficult, even if the charge and discharge treatment step (III) is performed by increasing the charging voltage to 3.5 V, to attain such a satisfactory charge and discharge capacity increasing effect that the discharge capacity per

25 weight at the charging at a constant current density with

the voltage gradually increased to 2.5 V can be increased as much as at least 10% when the specific surface area is in the range of 30 to 1000 m^2/g and as much as at least 3% when the specific surface area exceeds 1000 m^2/g and is up

5   to 1200 m^2/g.

Moreover, when the specific surface area exceeds 1200 m^2/g, the activation is time-consuming and the activation yield is lowered, so that attaining desired charge and discharge capacities per volume tends to be difficult.

10   In this specification, the specific surface area is a value measured by the BET method based on nitrogen adsorption and, taking measuring accuracy into account, expressed by three digits of significant figure (provided that, with respect to less than one hundred, fractions of .5

15   and over are counted as a unit and the rest is cut away).
2) Pore distribution of active carbon fiber:

The average pore radius of the active carbon fiber obtained by the activation step (II) of the present invention is preferably in the range of 0.2 to 1 nm, still

20   preferably 0.6 to 1 nm.

When the average pore radius exceeds 1 nm, the effect of increasing charge and discharge capacities, attained by the charge and discharge treatment step (III) described later, tends to be extremely slight.

On the other hand, when the average pore radius is less than 0.2 nm, the specific surface area is extremely small although the effect of increasing charge and discharge capacities in the charge and discharge treatment step (III)

5   is conspicuous with the unfavorable result that the absolute value of charge and discharge capacities of the active carbon fiber as a final product is small.

In the present invention, the average pore radius is a value calculated from t-plot of a nitrogen adsorption

10   isotherm at liquid nitrogen temperature, based on the results of the nitrogen adsorption method employed in the measuring of the BET specific surface area.

In the present invention, the mesophase pitch based active carbon fiber obtained in this activation step (II)

15   is subjected to specified charge and discharge treatment performed in the charge and discharge treatment step (III).

Charge and discharge treatment step (III)

In the charge and discharge treatment step (III) of the present invention, the active carbon fiber obtained in

20   the activation step (II) is immersed in an electrolyte and subjected to such a charge and discharge treatment that a voltage gradually increased until exceeding 2.5 V is applied at a constant current density to the active carbon fiber so that an electric double layer is formed at an

25   interface of the active carbon fiber and the electrolyte

to thereby effect a charging and thereafter a discharging is effected at a constant current density.

In this charge and discharge treatment step (III), the active carbon fiber may be used directly as an electrode in the formation of electric double layer, or may be mixed with a binder and molded into a molding (electrode) before the use in the formation of electric double layer, as described later.

In this charge and discharge treatment step (III), although any of common electrolytes can be employed, the use of organic nonaqueous electrolytes described below is especially preferred from the viewpoint that a high voltage can be applied.

Organic solvents for use in such organic nonaqueous electrolytes are not particularly limited and may be, for example, any of the organic solvents set forth later. However, it is especially preferred to employ organic polar solvents such as ethylene carbonate, γ-butyrolactone, sulfolane, dimethylformamide, 3-methylsulfolane and propylene carbonate.

Electrolytic substances for use in such electrolytes are not particularly limited and can be, for example, any of the salts described later. EtN_4BF_4 and $LiClO_4$ can be mentioned as preferred examples thereof.

In the use of an organic nonaqueous polar solvent such as propylene carbonate, the concentration of electrolytic substance is preferably in the range of 0.5 to 3 M/L, still preferably 1 to 2 M/L.

5   In the charge and discharge treatment, the voltage applied to the active carbon fiber is gradually increased from the state of no voltage application to over 2.5 V, preferably over 2.5 V but not greater than 4.0 V, and still preferably 3.5 V.

10   The rate of voltage increase is so set that the density of current flowing through the electrode comprising the active carbon fiber is constant. This current density is preferably in the range of 0.1 to 100 mA/cm^2, still preferably 1 to 100 mA/cm^2.

15   The charge and discharge treatment step (III) of the present invention can be performed with the use of electric double layer capacitor (described later), for example, shown in appended Figs. 1A to 1C.

Specifically, in the charge and discharge treatment

20   step (III) using such electric double layer capacitor 1 shown in appended Figs. 1A to 1C, the mesophase pitch based active carbon fiber obtained in the activation step (II) is formed directly, or after being mixed with a binder and molded into, for example, a sheet, into electrodes 5,6 and

25   the charging and discharging are carried out so that the

charge and discharge treatment of the active carbon fiber is effected.

In this charge and discharge treatment, the charging is carried out in such a manner that the potential

5   difference between the electrodes 5,6 is gradually increased from the state of 0 V to over 2.5 V, especially preferably 3.5 V, so as to allow the current density to be constant and that, after the voltage reaches a given value, the voltage is maintained until a stable state is reached.

10   Thereafter, the discharging is conducted by controlling the velocity of drop of potential difference between the two electrodes so as to allow the current density to be constant.

The now apparent charge and discharge treatment step

15   (III) of the present invention realizes a marked increase of charge and discharge capacities per volume over those of the active carbon fiber having an equivalent specific surface area but not having undergone this treatment.

More specifically, the use of the active carbon fiber

20   obtained in the activation step (II) as electrodes of an electric double layer capacitor and subjected to the charge and discharge step (III) by increasing the charging voltage to, for example, 3.5 V enables increasing the discharge capacity per weight, which is measured at the charging at

25   a constant current density with the voltage increased to

2.5 V, followed by the discharging at a constant current density (for example, the current density at charging and discharging: 100 mA/cm^2), as much as at least 10% when the specific surface area is in the range of 30 to 1000 m^2/g

5   and as much as at least 3% when the specific surface area exceeds 1000 m^2/g and is up to 1200 m^2/g.

The discharge capacity per weight of the active carbon fiber can be measured by the use of, for example, electric double layer capacitor shown in appended Figs. 1A to 1C

10   along with the electrolyte selected from among those examples set forth in the above charge and discharge treatment.

Specifically, the active carbon fiber to be measured with respect to the charge and discharge capacities,

15   directly or after being mixed with a binder and molded into, for example, a sheet, is used as electrodes 5,6 of electric double layer capacitor 1 shown in appended Figs. 1A to 1C. The charging is carried out in such a manner that the potential difference between the electrodes 5,6 is

20   gradually increased from the state of 0 V to 2.5 V so as to allow the current density to be constant and that, after the voltage reaches a given value, the voltage is maintained until a stable state is reached. Thereafter, the discharging is conducted by controlling the velocity of

drop of potential difference between the two electrodes so as to allow the current density to be constant.

The discharge capacity of the electrodes 5,6 is calculated from the slope of discharge curve (curve showing

5   the potential difference between the two electrodes vs. discharging time) obtained by the above charging and discharging. The discharge capacity per weight (F/g) can be determined from the calculated value and the total weight of active carbon fiber used as the electrodes 5,6.

10   With respect to the mesophase pitch based active carbon fiber, it has been believed that the charge and discharge capacity per weight is highly associated with the specific surface area and pore distribution.

It has also been believed that an active carbon fiber

15   of large specific surface area (generally at least 2000 m^2/g) in which pores with a certain specified size for permitting infiltration of an electrolyte (generally having an average pore radius of at least 1 nm) are distributed in a large proportion is desirable for use as

20   an electrode material of electric double layer capacitor.

However, the inventors' investigations have revealed that the mesophase pitch based active carbon fiber obtained in the activation step (II), when having a small specific surface area as measured by the BET method (up to 1200 m^2/g,

25   especially up to 1000 m^2/g) and when containing micropores

having been regarded as being unsuitable to the formation

of an electric double layer in a large proportion and thus

having a small average pore radius calculated from t-plot

of a nitrogen adsorption isotherm (average pore radius: 0.2

5   to 1 nm), exhibits a marked effect of increasing charge and

discharge capacities in the charge and discharge treatment

step (III). Although, when the active carbon fiber having

been subjected to the charge and discharge treatment step

(III) is subjected to the charge and discharge treatment

10   step (III) once more, the increasing effect is not so high

as in the initial treatment, substantially constant high

charge and discharge capacities can be maintained

thereafter under regular charging and discharging

conditions. Despite these, after the charge and discharge

15   treatment step (III), there is no significant change

recognized in the specific surface area and average pore

radius of the active carbon fiber, measured by the

aforementioned methods.

With respect to this phenomenon, although the clear

20   cause thereof has not yet been elucidated, it can be

presumed that some change exerting no significant influence

on the average pore radius and specific surface area is made

on the structure and/or internal-surface properties of

pores with small radii which are originally not associated

25   with the formation of electric double layer by virtue of

the charge and discharge treatment performed at a high

voltage exceeding 2.5 V in the charge and discharge

treatment step (III) with the result that these small pores

come to contribute to charge and discharge capacities in

5   cooperation with the pores with large radii so as to realize

a marked increase of charge and discharge capacities.

The mesophase pitch based active carbon fiber of the

present invention can be produced by the above process of

the present invention.

10   The mesophase pitch based active carbon fiber of the

present invention preferably has an average pore radius,

calculated from t-plot of a nitrogen adsorption isotherm,

of 0.2 to 1 nm, still preferably 0.6 to 1.0 nm.

The employment of an average pore radius of less than

15   0.2 nm, although the increase of capacitor capacity at high

voltage is large, is unfavorable because the specific

surface area becomes extremely small to thereby reduce the

absolute value of capacitor capacity. The upper limit of

average pore radius of the mesophase pitch based active

20   carbon fiber of the present invention is determined on the

grounds that, with the use of an active carbon fiber of over

1 nm, it is difficult to attain the effect of increasing

charge and discharge capacities in the charge and discharge

treatment step (III).

The mesophase pitch based active carbon fiber of the present invention preferably has a discharge capacity per weight, exhibited when an electric double layer is formed, of 20 to 45 F/g, still preferably 30 to 45 F/g.

5   The electric double layer capacitor of the present invention includes the electrode comprising the above mesophase pitch based active carbon fiber.

In the present invention, the method of preparing the electrode is not particularly limited, and any of

10   conventional electrode producing techniques can be used without modification.

For example, the electrode of the present invention can be produced by adding a binder such as polyethylene, polytetrafluoroethylene (PTFE) or polyvinylidene fluoride

15   (PVDF) to the mesophase pitch based active carbon fiber, mixing them and forming the resultant mixture into a sheet or a plate by means of a pressure roller.

During the production of the electrode, for example, graphite powder or carbon blacks such as acetylene black

20   can be added as a conductive material. Further, the mesophase pitch based active carbon fiber having the form of a mat or a felt can be coated with a conductive material such as aluminum by vapor deposition and formed into an electrode in order to enhance the current collectivity of

the electrode.   Still further, the active carbon fiber can be formed into paper and thereafter into an electrode.

A single-pole cell can be prepared by cutting the thus obtained electrode into desired size and shape, interposing
5   a separator between counter electrodes, inserting them into a casing, injecting an electrolyte thereinto and caulking closure with the use of closing plates and gaskets.

It is preferred to employ an organic solvent type electrolyte to which a high voltage can be applied as the
10   electrolyte for use in the electric double layer capacitor.

Examples of suitable organic solvents include propylene carbonate, γ-butyrolactone, dimethyl sulfoxide, dimethylformamide, acetonitrile, ethylene carbonate, tetrahydrofuran and dimethoxyethane.
15   These organic solvents can be used either individually or in combination (mixture).

Examples of suitable electrolytic substances to be dissolved in these solvents include metal cations; quaternary ammonium cations such as ammonium ion,
20   tetramethylammonium ion and tetraethylammonium ion; and salts of cations such as carbonium cation and appropriate anions.

Examples of such anions include ClO_4^-, BF_4^-, PF_4^-, PF_6^- and AsF_6^-.

Specific examples of electrolytic substances include $LiClO_4$, $BuN \cdot ClO_4$, $NaBF_4$ and EtN_4BF_4 (in the formula, Et represents ethylene).

In the use of an organic nonaqueous polar solvent, the

5   concentration of electrolytic substance is preferably in the range of 0.5 to 3 M/L, still preferably 1 to 2 M/L.

The structure of representative electric double layer capacitor in which the present invention is utilized will now be described.

10 Figs. 1A to 1C show an embodiment of electric double layer capacitor of the present invention. As shown, the electric double layer capacitor 1 comprises two pressure boards 3,4 and, interposed therebetween, a pair of electrodes 5,6.

15 Aluminum meshes 7,8 are bonded to the electrodes 5,6 at their pressure board sides, respectively. Ends of aluminum wires 9,10 are welded to the aluminum meshes, respectively. Separator 11 is interposed between the electrodes 5,6.

20 Each of the pressure boards 3,4 is provided with four fixing protrusions 12,12,.. which protrude outwards from both side edges. The electrode sheets and separator are fixed between the pressure boards by polyester (Tetron) bands 13,13,.. wound round the protrusions 12,12,.., and

25 immersed in the electrolyte.

(EFFECT OF THE INVENTION)

By virtue of the foregoing process for producing a mesophase pitch based active carbon fiber and mesophase

5   pitch based active carbon fiber according to the present invention, there can be provided a process for producing an active carbon fiber which, when used as an electrode material, not only can realize a high bulk density because of the small specific surface area but also exhibits

10   excellent charging and discharging performance, especially capable of realizing large charge and discharge capacities per weight and per volume, and further there can be provided such an active carbon fiber and an electrode for electric double layer capacitor in which the active carbon fiber is

15   used.

(EXAMPLE)

The present invention will further be illustrated below with reference to the following Examples which in no

20   way limit the scope of the invention.

(Example 1)

Mesophase pitch having a Mettler softening point of 285°C, obtained by conducting a thermal treatment of cracked petroleum residue, was melt-blowing spun through

25   a nozzle having a 2 mm wide slit in which a line of 1000

spinning orifices each having a diameter of 0.2 mm are arranged, to thereby obtain pitch fibers. The spun pitch fibers were collected on a belt having a collection zone of 35-mesh stainless steel net while sucking from the back

5 of the belt.

The resultant collected pitch fiber mat was infusibilized in air at an average temperature rising rate of 4°C/min to thereby obtain infusibilized fibers. The infusibilized fibers were carbonized at 650°C in nitrogen

10 gas and pulverized (milled) with the use of high-speed rotary mill so that the average particle size became 25 µm.

Potassium hydroxide was added to the milled carbon fibers in a weight ratio of 2:1 (potassium hydroxide : carbon fibers), homogeneously mixed and heated at 700°C in

15 a nitrogen atmosphere for 2 hours to thereby effect an activation of the carbon fibers. Subsequently, cooling was made to room temperature, and the reaction product was poured into isopropyl alcohol. Thereafter, washing with water was performed until neutrality. Thus, active carbon

20 fibers having a BET specific surface area of 850 m^2/g were obtained.

The yield of active carbon fibers was as high as 77 wt.%.

The average pore radius of the active carbon fibers

25 was 0.82 nm.

The properties of obtained active carbon fibers are listed in Table 1.

80 parts by weight of obtained active carbon fibers, 15 parts by weight of carbon black as a conductive material

5 and 5 parts by weight of PTFE as a binder were mixed together. The thus obtained mixture was rolled into a sheet (thickness: 70 to 100 μm and electrode area: 2.5 cm^2). Pieces of the resultant sheet were compression bonded to aluminum meshes, thereby obtaining electrodes. An

10 electric double layer capacitor was prepared by using the obtained electrodes as positive and negative electrodes 5,6 as shown in Figs. 1A to 1C, interposing a filter paper as a separator between the electrodes and charging an electrolyte composed of propylene carbonate containing 1

15 M lithium perchlorate as an electrolytic substance.

The potential difference between the electrodes 5,6 of this electric double layer capacitor was gradually increased from the state of 0 V to 2.5 V and to 3.5 V so so as to make each of the current densities 100 mA/cm^2. Upon

20 reaching of the voltage to given value, discharging was effected at the same current density. The discharge capacity per weight (F/g) was measured with respect to each of the applied voltages.

Using an electric double layer capacitor prepared in

25 the same manner, the potential difference between the

electrodes 5,6 thereof was gradually increased from the state of 0 V to 3.5 V so as to make the current density 100 mA/cm^2. Upon reaching of the voltage to given value, discharging was effected at the same current density to

5   thereby carry out a charge and discharge treatment. Thereafter, in the same manner, the discharge capacity per weight (F/g) was measured at an applied voltage of 2.5 V.

The obtained results are given in Table 1.

As seen from Table 1, the discharge capacity exhibited

10   when the charging was performed at an applied voltage of 2.5 V was 26.3 F/g, while the discharge capacity exhibited when the charging was performed at an applied voltage of 3.5 V was 36.5 F/g. On the other hand, after the charge and discharge treatment at an applied voltage of 3.5 V, the

15   discharge capacity exhibited when the charging was performed at an applied voltage of 2.5 V was 36.3 F/g. Thus, the discharge capacity after the charge and discharge treatment was 38.0% greater than that without the treatment.

20   (Comparative Example 1)

Active carbon fibers having a specific surface area of 880 m^2/g were produced in the same manner as in Example 1, except that optically isotropic pitch having a Mettler softening point of 270°C, obtained by conducting a thermal

25   treatment of cracked petroleum residue, was used as the

pitch material. An electric double layer capacitor was prepared with the use of the active carbon fibers in the same manner as in Example 1, and the capacities of the capacitor were measured.

5   The results are also given in Table 1.

As seen from Table 1, the discharge capacity exhibited when the charging was performed at an applied voltage of 2.5 V was equivalent to that of Example 1. However, as different from Example 1, the discharge capacity increasing

10   effect of the charge and discharge treatment at an applied voltage of 3.5 V was not recognized at all.

Table 1

	Example 1	Comp. Ex. 1

Carbon fiber
  raw material pitch
  carbonization temp. (°C)
	mesophase pitch
	650
		isotropic pitch
		650

Alkali activation
  activation temp. (°C)
  activation time (hr)
  amt. of KOH (wt. ratio to CF)
	700
	2
	2
		700
		2
		2

Properties of active carbon fiber
  sp. surface area (m^2/g)
  av. pore radius (nm)
  yield (vs. CF) (wt.%)
	850
	0.82
	77
		880
		1.05
		72

Properties of capacitor discharge capacity at 2.5 V charging (C_A) (F/g)	26.3	26.9
discharge capacity at 3.5 V charging (C_B) (F/g)	36.5	27.0
discharge capacity at 2.5 V charging (C_C) (F/g) after 3.5 V charge and discharge treatment	36.3	26.9
Capacity increase (%) (C_C-C_A)÷C_Ax100	38.0	0

(Example 2 and Referential Example 1)

Four varieties of active carbon fibers were produced
in the same manner as in Example 1, except that the
temperature for carbonizing the infusibilized fibers
obtained in Example 1 in nitrogen gas was changed as
specified in Table 2. Thereafter, electric double layer
capacitors were prepared by way of trial with the use of
the active carbon fibers and the capacities of the
capacitors were measured, in the same manner as in Example
1.

The results are collectively given in Table 2.

Table 2

		Example 2		Ref. Ex. 1	
Carbon fiber raw material pitch		mesophase pitch			
carbonization temp. (°C)		750	850	570	930
Alkali activation activation temp. (°C) activation time (hr) amt. of KOH (wt. ratio to CF)		700 2 2	700 2 2	700 2 2	700 2 2
Properties of active carbon fiber sp. surface area (m^2/g) av. pore radius (nm) yield (vs. CF) (wt.%)		70 0.95 80	35 0.79 85	1050 1.03 70	16 0.82 85
Properties of capacitor discharge capacity at 2.5 V charging (C_A) (F/g)		5.5	4.0	29.0	1.9
discharge capacity at 3.5 V charging (C_B) (F/g)		26.2	22.4	30.0	14.2
discharge capacity at 2.5 V charging (C_C) (F/g) after 3.5 V charge and discharge treatment		25.9	21.6	29.6	13.2
Capacity increase (%) $(C_C - C_A) \div C_A \times 100$		371	440	2.1	594

(Example 3 and Comparative Example 2)

Using the carbon fibers obtained at a carbonization temperature of 750 °C in the same manner as in Example 2, two varieties of active carbon fibers having different specific surface areas were produced in the same manner as in Example 1, except that the conditions for alkali activation of the carbon fibers were changed as specified in Table 3. Thereafter, electric double layer capacitors were prepared with the use of the active carbon fibers, and the capacities of the capacitors were measured, in the same manner as in Example 1.

43

The results are collectively given in Table 3.

Table 3

5

	Example 3	Comp. Ex. 2
Carbon fiber raw material pitch carbonization temp. (°C)	mesophase pitch 750	
Alkali activation activation temp. (°C) activation time (hr) amt. of KOH (wt. ratio to CF)	700 2 4	700 1 1
Properties of active carbon fiber sp. surface area (m^2/g) av. pore radius (nm) yield (vs. CF) (wt.%)	400 0.83 73	20 0.78 88
Properties of capacitor discharge capacity at 2.5 V charging (C_A) (F/g)	26.2	1.2
discharge capacity at 3.5 V charging (C_B) (F/g)	41.7	13.5
discharge capacity at 2.5 V charging (C_C) (F/g) after 3.5 V charge and discharge treatment	40.5	12.6
Capacity increase (%) (C_C-C_A)÷C_Ax100	54.9	950